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The Synthesis of 1-Phenylazulene and 2-Phenylazulene from the Troponoid Compound

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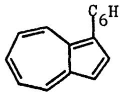
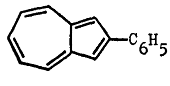
1-Phenylazulene (I) and 2-phenylazulene (II) were synthesized from the troponoid compound. 3-Phenyl-(III) and 3-benzoyl-2*H*-cyclohepta[*b*]furan-2-ones (IV) were prepared by the reaction of 2-chlorotropone with ethyl phenylacetate and with ethyl benzoylacetate respectively. The reactions of III with malononitrile or ethyl cyanoacetate gave 1-phenylazulene derivatives, from which I was derived. On the other hand, the reactions of IV with ethyl cyanoacetate or diethyl malonate gave 2-phenylazulene derivatives, from which II was derived.

As has been described in previous papers,[1,2] it has been found that the reaction of 2*H*-cyclohepta[*b*]furan-2-one derivatives with compound having a reactive methylene group, such as malononitrile, ethyl cyanoacetate, or diethyl malonate, gave azulene derivatives bearing the substituents at the 1-, 2-, and 3-positions. Moreover, the relationship between the kinds of substituents in the azulene derivatives formed and the structures of the starting 2*H*-cyclohepta[*b*]furan-2-one derivatives or of the compounds with the reactive methylene group has also been revealed.[2] These findings suggest that this reaction can be used fruitfully in the synthesis of azulene derivatives bearing the desired substituents. As an application of this reaction, we have now studied the synthesis of 1-phenylazulene(I) and 2-phenylazulene(II) from the troponoid compound, though I has been synthesized by Plattner *et al.*[3] from bicyclo[5,3,0]decenone and by Hafner[4] through the condensation of the cyclopentadiene derivative and pyridinium salt, and II has also been synthesized by Plattner *et al.*[3] from phenylindane.

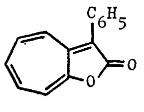
Considering the reaction mechanism[2] of the formation of azulene derivatives from 2*H*-cyclohepta[*b*]furan-2-one derivatives, it is expected that 1-phenyl- and 2-phenylazulene derivatives should be formed from 3-phenyl- (III) and 3-benzoyl-2*H*-cyclohepta[*b*]furan-2-ones (IV) respectively by means of reactions analogous to those in the formations of the azulene-1-carboxylic esters (VIa) or 2-methylazulene derivatives (VIb) from 3-ethoxycarbonyl- (Va) or 3-acetyl-2*H*-cyclohepta[*b*]furan-2-ones (Vb)[2] respectively. Consequently, compounds III and IV



I



II



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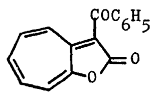
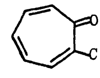
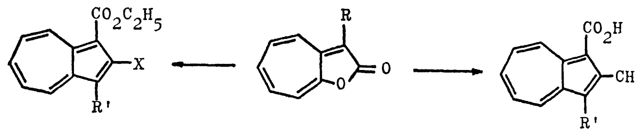


IV



VII



VIa: $R'=CN$ or $CO_2C_2H_5$
$X=NH_2$ or OH

Va: $R=CO_2C_2H_5$
Vb: $R=COCH_3$

VIb: $R'=CN$ or $CO_2C_2H_5$

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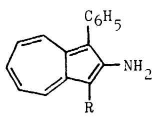
[1] T. Nozoe, K. Takase, and N. Shimazaki, This Bulletin, **37**, 1644 (1964).

[2] T. Nozoe, K. Takase, T. Nakazawa, and S. Fukuda, *Tetrahedron*, to be published.

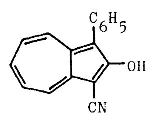
[3] Pl. A. Plattner, R. Sandrin, and J. Wyss, *Helv. Chim. Acta*, **29**, 1604 (1946); Pl. A. Plattner, A. Fürst, M. Gordon, and K. Zimmermann, *ibid.*, **33**, 1910 (1950).

[4] K. Hafner, *Angew. Chem.*, **67**, 301 (1955).

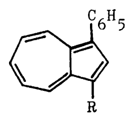
should be important intermediates in the synthesis of 1-phenylazulene(I) and 2-phenylazulene(II) from the troponoid compound. Moreover, compounds III and IV are expected to be prepared from 2-chlorotropone(VII)[5] in a way analogous to the preparation of Va and Vb.[6]



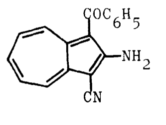
VIIIa: R=CN
VIIIb: R=$CO_2C_2H_5$



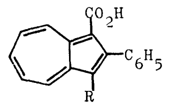
IX



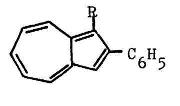
Xa: R=CN
Xb: R=$CO_2C_2H_5$



XI



XIIa: R=CN
XIIb: R=$CO_2C_2H_5$



XIIIa: R=CN
XIIIb: R=$CO_2C_2H_5$
XIV: R=$CONH_2$

Results and Discussion

1-Phenylazulene. In order to prepare 3-phenyl-2*H*-cyclohepta[*b*]furan-2-one(III), the reaction of 2-chlorotropone(VII) with ethyl phenylacetate was examined. This reaction succeeded in the presence of sodium ethoxide, giving III in an 81% yield. The structure of III was revealed from the fact that its ultraviolet spectrum is similar to those of 2*H*-cyclohepta[*b*]furan-2-one derivatives,[6] while its infrared spectrum shows absorptions at 1736 and 1721 cm^{-1}, corresponding to those of the five-membered lactone.

Compound III easily reacted with malononitrile in the presence of sodium ethoxide to give an azulene derivative(VIIIa) in a good yield. The reaction of III with ethyl cyanoacetate also proceeded easily in the presence of sodium ethoxide to afford a mixture of a basic azulene derivative(VIIIb) and an acidic azulene derivative(IX). On the other hand, the reaction of III with diethyl malonate ended in the recovery of the original substance. The azulene derivatives obtained here, VIIIa, VIIIb, and IX, were assigned the structures of 2-amino-1-cyano-3-phenylazulene, ethyl 2-amino-3-phenylazulene-1-carboxylate and 1-cyano-2-hydroxy-3-phenylazulene respectively on the basis of a consideration of a reaction mechanism for their formation analogous to that for the formation of azulene derivatives from 2*H*-cyclohepta[*b*]furan-2-one derivatives,[2] as well as on the basis of the observations to be described below. The ultraviolet and visible absorption spectra revealed these compounds to be azulene derivatives. Their infrared spectra show the characteristic absorptions as shown in Table 1. Moreover, VIIIa gave a *N*-acetyl derivative, VIIIb gave a picrate, and IX gave a methyl ether with diazomethane.

Table 1. The infrared spectral data of the azulene derivatives

Compound	Absorptions, cm^{-1} (KBr)
VIIIa	3410, 3300, 3185 (NH_2); 2198 (CN)
IX	3135 (OH); 2222 (CN)
XI	3410, 3330, 3205 (NH_2); 2212 (CN); 1603 (CO)
XIIa	3330∼2400, 1647, 931 (CO_2H); 2217 (CN)
Me ester of XIIa	2217 (CN), 1692 (CO)
XIIb	3165 (broad), 1647, 927 (CO_2H); 1698 (CO)
Me ester of XIIb	1678 (CO)

The treatment of VIIIa and of VIIIb with isoamyl nitrite in the presence of sulfuric acid in ethanol-dioxane gave deamination products, (Xa) and (Xb) respectively. Their infrared spectra show absorptions at 2208 and 1684 cm^{-1}, corresponding to those of the conjugated cyano and carbonyl groups respectively. The deamination of VIIIa was rather difficult; it produced a slightly soluble, black material, together with Xa. Upon heating in 100% phosphoric acid, both Xa and Xb gave the same blue hydrocarbon. Although its melting point, 61—62°C, was higher than that previously reported,[3] 54—55°C, its ultraviolet and visible absorption spectra and infrared spectrum were identical with those of 1-phenylazulene (I).[3] Moreover, the melting point of bistrinitrobenzolate was also identical with that of I.

2-Phenylazulene. 3-Benzoyl-2*H*-cyclohepta[*b*]furan-2-one (IV) was obtained in a 66% yield by the reaction of 2-chlorotropone (VII) with ethyl benzoylacetate in the presence of sodium ethoxide. The ultraviolet spectrum is similar to those of 2*H*-cyclohepta[*b*]-furan-2-one derivatives,[6] and the infrared spectrum shows an absorption at 1773 cm^{-1} corresponding to that of the five-membered lactone. These spectral data are consistent with the structure of IV.

Compound IV easily reacted with malononitrile in the presence of tert-butylamine to give a basic azulene derivative(XI). The reaction of IV with ethyl cyanoacetate and with diethyl malonate also proceeded easily in the presence of sodium ethoxide to give acidic azulene derivatives, XIIa and XIIb respectively. These azulene derivatives, XI, XIIa, and XIIb, were assigned the structures of 2-amino-1-benzoyl-3-cyanoazulene, 3-cyano-2-phenylazulene-1-carboxylic acid, and 3-ethoxycarbonyl-2-phenylazulene-1-carboxylic acid respectively on the basis of a consideration of the reaction mechanism for their formation analogous to that established for the formation of azulene derivatives from 2*H*-cyclohepta[*b*]furan-2-one derivatives,[2] as well as on the basis of the observations to be described below. The ultra-

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[5] T. Nozoe, S. Seto, H. Takeda, S. Morosawa, and K. Matsumoto, *Sci. Repts. Tohoku Univ., Ser. I*, **36**, 126 (1952); S. Seto, *ibid.*, **37**, 275 (1953); B. J. Abadir, J. W. Cook, J. D. Loudon, and D. D. V. Steel, *J. Chem. Soc.*, **1952**, 2350; W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, **74**, 5683 (1952); W. von E. Doering and C. F. Hiskey, *ibid.*, **74**, 5688 (1952).

[6] S. Seto, *Sci. Repts. Tohoku Univ., Ser. I*, **37**, 367 (1953).

violet and visible absorption spectra revealed these compounds to be azulene derivatives. Their infrared spectra show the characteristic absorptions shown in Table 1. Moreover, compound XI gave a *N*-acetyl derivative upon treatment with acetic anhydride, and gave 2-amino-1-cyanoazulene,[2] identified as the *N*-acetyl derivative, and benzoic acid upon heating in concentrated hydrobromic acid. On the other hand, compounds XIIa and XIIb, which were assumed to be carboxylic acids on the basis of their infrared spectra, were soluble in a sodium hydrogen carbonate solution and gave the corresponding methyl esters on methylation with diazomethane.

The derivation of 2-phenylazulene(II) from XIIa was achieved by a two-step procedure. Thus, XIIa gave 1-cyano-2-phenylazulene (XIIIa) or 1-carbamoyl-2-phenylazulene(XIV) upon heating in 100% phosphoric acid or in concentrated sulfuric acid respectively. The infrared spectra of XIIIa and XIV show the absorptions at 2208 cm^{-1} and at 3367, 3155, and 1631 cm^{-1}, corresponding to the conjugated cyano and carbamoyl groups respectively. The further treatment of XIV with 100% phosphoric acid gave a blue hydrocarbon in a good yield; it was identified with 2-phenylazulene (II)[3] on the basis of a comparison of the ultraviolet and visible absorption spectra and on the basis of the infrared spectra. On the contrary, the treatment of XIIIa in concentrated sulfuric acid gave mainly XIV, together with a small amount of II.

On the other hand, compound XIIb gave II directly and in a good yield upon heating in 100% phosphoric acid. However,when heated in concentrated hydrobromic acid, XIIb gave ethyl 2-phenylazulene-1-carboxylate (XIIIb) by decarboxylation, together with II. Compound XIIIb easily gave II in a good yield when heated in 100% phosphoric acid.

As has been described above, 1-phenylazulene(I) and 2-phenylazulene(II) were easily synthesized from troponoid compounds in good yields. Moreover, this synthetic procedure is thought to be desirable since all the steps proceeded under rather mild conditions; consequently, there is no trouble in the thermal isomerization between I and II at high temperatures.[3]

Experimental

All the melting points are uncorrected. The ultraviolet and visible absorption spectra were measured on a Hitachi EPS-3 spectrophotometer, while the infrared spectra were recorded on a Shimadzu IR-27 infracord apparatus.

*3-Phenyl-2*H*-cyclohepta*[b]*furan-2-one (III).* Into a solution of 2-chlorotropone(VII) (2.80 g) and ethyl phenylacetate (6.60 g) in anhydrous ethanol (15 m*l*), a sodium ethoxide solution prepared from sodium (920 mg) and anhydrous ethanol (20 m*l*) was stirred under cooling with ice water. After having been stirred for an additional 2 hr, the mixture was allowed to stand for 2 days in a refrigerator and then poured into water (300 m*l*). The crystals thereby formed were collected by filtration. Yield, 3.59 g; mp 135—140°C. Recrystallization from ethanol gave III as reddish-orange needles; mp 146—147°C.

Found: C, 81.27; H, 4.60%. Calcd for $C_{15}H_{10}O_2$: C, 81.06; H, 4.54%. UV (MeOH): λ_{max} nm (log ε); 226 (4.48), 265 (4.40), 400 (4.28).

2-Amino-1-cyano-3-phenylazulene (VIIIa). To a solution of III (380 mg) and malononitrile (200 mg) in anhydrous ethanol (5 m*l*), 1 M sodium ethoxide solution (3 m*l*) was added; the mixture was stirred for 2 hr and then allowed to stand for 2 days at room temperature. Water was added to this mixture, and the crystals thereby formed were collected by filtration to give VIIIa (390 mg); mp 190—193°C. Recrystallization from dioxane afforded red micro-needles; mp 195—196°C.

Found: C, 83.17; H, 4.63; N, 11.20%. Calcd for $C_{17}H_{12}N_2$: C, 83.58; H, 4.95; N, 11.47%. UV (MeOH): λ_{max} nm (log ε); 247 (4.44), 316 (4.76), 380 (4.02).

N-*Acetyl Derivative*: Violet prisms (from dimethylformamide); mp 225—226°C.

Found: C, 79.66; H, 5.05; N, 9.50%. Calcd for $C_{19}H_{14}ON_2$: C, 79.70; H, 4.93; N, 9.78%. UV (MeOH): λ_{max} nm (log ε); 246 (4.40), 314 (4.75), 357 (3.82), 545 (2.79).

Ethyl 2-Amino-3-phenylazulene-1-carboxylate (VIIIb) and 1-Cyano-2-hydroxy-3-phenylazulene (IX). To a solution of III (380 mg) and ethyl cyanoacetate (480 mg) in anhydrous ethanol (6 m*l*), a 1 M sodium ethoxide solution (8 m*l*) was added; the mixture was stirred for 2 hr and then allowed to stand for 2 days at room temperature. The reaction mixture was then poured into water and shaken with chloroform. The chloroform layer was dried over anhydrous sodium sulfate, after which the solvent was evaporated. The oily residue was solidified by the addition of ethanol, giving VIIIb (260 mg); mp 121—122°C. Recrystallization from ethanol gave red prisms; mp 124—125°C.

Found: C, 78.14; H, 5.79; N, 4.49%. Calcd for $C_{19}H_{17}O_2N$: C, 78.33; H, 5.88; N, 4.81%. UV (MeOH): λ_{max} nm (log ε); 255 (4.43), 320 (4.58).

Picrate: Violet needles (from ethanol); mp 137—138°C.

Found: C, 58.08; H, 3.86; N, 10.41%. Calcd for $C_{25}H_{20}O_9N_4$: C, 57.69; H, 3.87; N, 10.77%.

The aqueous layer was acidified with 6 N hydrochloric acid, and the crystals thereby formed were collected by filtration to give IX (130 mg); mp 213—216°C. Recrystallization from dioxane gave reddish brown micro-needles; mp 232—233°C.

Found: C, 80.71; H, 4.82; N, 5.35%. Calcd for $C_{17}H_{11}ON\text{-}1/2H_2O$: C, 80.30; H, 4.76; N, 5.51%. UV (MeOH): λ_{max} nm (log ε): 247 (4.50), 314 (4.70), 449 (2.77).

Methyl Ether: Reddish violet needles (from ethanol); mp 136—137°C.

Found: C, 83.19; H, 5.26; N, 5.15%. Calcd for $C_{18}H_{13}ON$: C, 83.37; H, 5.05; N, 5.40%. UV (MeOH): λ_{max} nm (log ε); 245 (4.37), 308 (4.66). 358 (3.61), 400 sh (3.11), 503 (2.57).

1-Cyano-3-phenylazulene (Xa). To a solution of VIIIa (470 mg) in a mixture of ethanol (6 m*l*) and dioxane (6 m*l*) containing concentrated sulfuric acid (0.4 m*l*), isoamyl nitrite (0.3 m*l*) was added; the mixture was then stirred for 5 hr at room temperature. The reaction mixture was then poured into water, extracted with chloroform, and dried over anhydous sodium sulfate. After the evaporation of the solvent, the residue was dissolved in benzene and passed through a short column of alumina. The evaporation of the solvent from the effluent left blue crystals (200 mg), mp 117—122°C, which were recrystallized from ethanol to give Xa as blue needles; mp 127—128°C.

Found: C, 89.37; H, 4.69; N, 5.94%. Calcd for C_{17}-

$H_{11}N$: C, 89.05; H, 4.84; N, 6.11%. UV (MeOH): λ_{max} nm (log ε); 241 (4.52), 300 (4.55), 375 (3.87), 570 (3.31).

Ethyl 3-Phenylazulene-1-carboxylate (Xb). To a solution of VIIIb (725 mg) in a mixture of ethanol (10 m*l*) and dioxane (6 m*l*) containing concentrated sulfuric acid (0.5 m*l*), isoamyl nitrite (0.4 m*l*) was added; when the mixture was then treated in a manner similar to that described above, it gave violet crystals (390 mg), mp 74—76°C. Recrystallization from ethanol gave Xb as violet scales; mp 82—83°C

Found: C, 82.87; H, 5.76%. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84%. UV (MeOH): λ_{max} nm (log ε); 243 (4.56), 285 (4.66), 303 (4.68), 382 (4.08), 560 (2.65).

1-Phenylazulene (I). *a) From Xa*: A mixture of Xa (100 mg) and 100% phosphoric acid (1 m*l*) was heated at about 120°C for 40 min, and then poured into water and extracted with chloroform. After drying over anhydrous sodium sulfate, the solvent was evaporated, and the oily residue was dissolved in benzene and chromatographed through an alumina column. The first effluent gave blue crystals (40 mg); mp 53—55°C. Recrystallization from ethanol gave I as blue scales; mp 61—62°C. The melting point previously reported was 54—55°C.[3]

Found: C, 93.97; H, 6.25%. Calcd for $C_{16}H_{12}$: C, 94.08; H, 5.92%. UV (MeOH): λ_{max} nm (log ε); 238 (450), 294 (4.62), 353 (3.83), 369 (3.84), 435 (2.08), 466 (2.13).

From the second effluent of the chromatography, Xa (37 mg) was recovered.

b) From Xb: A mixture of Xb (200 mg) and 100% phosphoric acid (2 m*l*) was heated at about 100°C for 1 hr, and then treated in a manner similar to that described above. The effluent of the chromatography gave blue crystals (142 mg), mp 57—59°C, which were recrystallized from ethanol to give I as blue scales, mp 61—62°C.

*3-Benzoyl-2*H*-cyclohepta*[b]*furan-2-one (IV).* Into a solution of 2-chlorotropone (VII) (3.5 g) and ethyl benzoylacetate (7.2 g) in anhydrous ethanol (10 m*l*), a 1 M sodium ethoxide solution was stirred under cooling with ice water. After stirring for an additional 2 hr, the mixture was allowed to stand overnight in a refrigerator and then poured into water (200 m*l*). The crystals thereby formed were collected by filtration and washed with a small amount of acetic acid, thus giving crude IV (4.1 g), mp 137—145°C. Recrystallization from glacial acetic acid afforded yellow prisms; mp 157—158°C.

Found: C, 76.81; H, 4.29%. Calcd for $C_{16}H_{10}O_3$: C, 76.79; H, 4.03%. UV (MeOH): λ_{max} nm (log ε); 227 (4.34), 257 (4.43), 427 (4.40).

2-Amino-1-benzoyl-3-cyanoazulene (XI). To a suspension of IV (500 mg) and malononitrile (200 mg) in anhydrous ethanol (5 m*l*), *t*-butylamine (15 drops) was added; the mixture was stirred for 5 hr at room temperature and then allowed to stand overnight. Water (30 m*l*) was added to this mixture, and the crystals thereby formed were collected by filtration, giving XI (520 mg); mp 214°C. Recrystallization from pyridine afforded orange micro-scales; mp 214—215°C.

Found: C, 79.26; H, 4.55; N, 9.98%. Calcd for $C_{18}H_{12}ON_2$: C, 79.39; H, 4.44; N, 10.29%. UV (MeOH): λ_{max} nm (log ε); 227 (4.37), 249 (4.24), 292 (4.47), 338 (4.48), 470 (3.43).

N-*Acetyl Derivative*: Orange needles (from dimethylformamide); mp 209—210°C.

Found: C, 76.39; H, 4.41; N, 9.01%. Calcd for $C_{20}H_{14}O_2N_2$: C, 76.42; H, 4.49; N, 8.91%. UV (MeOH): λ_{max} nm (log ε); 225 (4.36), 305 (4.62), 370 (3.91), 480 (2.79).

3-Cyano-2-phenylazulene-1-carboxylic Acid (XIIa). To a suspension of IV (250 mg) and ethyl cyanoacetate (230 mg) in anhydrous ethanol (3 m*l*), a 1 M sodium ethoxide solution (3 m*l*) was added; the mixture was stirred for 5 hr and then allowed to stand for 2 days at room temperature. The reaction mixture was dissolved in water (30 m*l*) and shaken with chloroform. The aqueous layer was acidified with 6 N hydrochloric acid, and the crystals thereby formed were collected by filtration, giving XIIa (250 mg); mp 228°C. Recrystallization from dioxane afforded red needles; mp 232—233°C.

Found: C, 78.88; H, 4.00; N, 4.90%. Calcd for $C_{18}H_{11}O_2N$: C, 79.11; H, 4.06; N, 5.13%. UV (MeOH): λ_{max} nm (log ε); 228 (4.40); 267 (4.32), 320 (4.69), 345 (3.91), 517 (2.74).

Methyl Ester. This ester was obtained by treatment of XIIa with diazomethane. Red micro-needles (from benzene); mp 173—174°C.

Found: C, 79.69; H. 4.57; N, 5.03%. Calcd for $C_{19}H_{13}O_2N$: C, 79.43; H, 4.56; N, 4.88%. UV (MeOH): λ_{max} nm (log ε); 230 (4.39), 269 (4.32), 320 (4.66), 525 (2.73).

3-Ethoxycarbonyl-2-phenylazulene-1-carboxylic Acid (XIIb). To a suspension of IV (500 mg) and diethyl malonate (0.65 m*l*) in anhydrous ethanol (8 m*l*), a 1 M sodium ethoxide solution (8 m*l*) was added; the mixture was then treated in a manner similar to that described above. The crude crystals (360 mg), mp 182°C (decomp.), obtained by the acidification of the aqueous layer were recrystallized from dioxane to give XIIb as red micro-needles; mp 190°C (decomp.).

Found: C, 71.39; H, 4.84%. Calcd for $C_{20}H_{16}O_4 \cdot H_2O$: C, 70.99; H, 5.36%. UV (MeOH): λ_{max} nm (log ε); 233 (4.34), 268 (4.24), 310 (4.60), 520 (2.70), 560 (2.69).

Methyl Ester. This ester was obtained by the treatment of XIIb with diazomethane. Red prisms (from methanol); mp 160—161°C.

Found: C, 75.45; H, 5.51%. Calcd for $C_{21}H_{18}O_4$: C, 75.43; H, 5.43%. UV (MeOH): λ_{max} nm (log ε); 233 (4.42), 273 (4.34), 305 (4.54), 515 (2.63).

Treatment of XI with Hydrobromic Acid. A mixture o XI (100 mg) and concentrated hydrobromic acid (1 m*l*) was heated at about 100°C for 2 hr, then diluted with water, made alkaline with 6 N potassium hydroxide solution, and extracted with chloroform. After drying over anhydrous sodium sulfate, the solvent was evaporated from the organic layer, the residue was heated with acetic anhydride (1 m*l*) for 15 min, and the crystals thereby formed were collected and recrystallized from ethyl acetate, thus giving 2-acetamido-1-cyanoazulene[2] (30 mg) as red needles; mp 225—226°C.

The alkaline aqueous layer was acidified with 6 N hydrochloric acid and extracted with chloroform. The solvent was evaporated, and the residue was sublimed under reduced pressure, thus giving benzoic acid (20 mg) as colorless crystals; mp 120—121°C.

1-Cyano-2-phenylazulene (XIIIa). A mixture of XIIa (100 mg) and 100% phosphoric acid (1 m*l*) was heated at about 100°C for 30 min, then diluted with water and extracted with benzene. The benzene solution was passed through a short column of alumina and the evaporation of the solvent from the effluent gave XIIIa (80 mg) as violet crystals; mp 110—111°C. Recrystallization from ethanol afforded violet plates; mp 115—116°C.

Found: C, 89.35; H, 4.80; N, 5.98%. Calcd for $C_{17}H_{11}N$: C, 89.05; H, 4.84; N, 6.11%. UV (MeOH): λ_{max} nm (log ε); 273 (4.22), 311 (4.24), 319 (4.78), 364

(3.93), 565 (2.78).

1-Carbamoyl-2-phenylazulene (XIV). A mixture of XIIa (100 mg) and concentrated sulfuric acid (1 m*l*) was heated at about 100°C for 40 min, and then diluted with water and extracted with chloroform. The chloroform solution was passed through a short column of alumina; the subsequent evaporation of the solvent from the effluent gave XIV (54 mg) as violet crystals, mp 186°C. Recrystallization from chloroform afforded violet plates; mp 189—190°C.

Found: C, 82.33; H, 5.16; N, 5.30%. Calcd for $C_{17}H_{13}ON$: C, 82.57; H, 5.30; N, 5.66%. UV (MeOH): λ_{max} nm (log ε); 243 (4.29), 303 (4.72), 310 (4.75), 364 (3.86), 383 sh (3.82), 565 (2.61).

2-Phenylazulene (II). a) Treatment of XIV with Phosphoric Acid: A mixture of XIV (35 mg) and 100% phosphoric acid (1 m*l*) was heated at about 100°C for 30 min, and then diluted with water and extracted with benzene. The benzene solution was passed through a short column of alumina; the subsequent evaporation of the solvent from the effluent gave II (20 mg) as blue crystals; mp 229°C. Recrystallization from benzene afforded blue plates; mp 231—232°C. The melting point previously reported[3] was 230°C.

Found: C, 94.08; H, 6.02%. Calcd for $C_{16}H_{12}$: C, 94.08; H, 5.92%. UV (isooctane): λ_{max} nm (log ε); 242 (4.11), 296 (4.79), 307 (4.81), 355 (3.73), 372 (4.05), 392 (4.19), 590 (2.46).

b) Treatment of XIIb with Phosphoric Acid: A mixture of XIIb (100 mg) and 100% phosphoric acid was heated at about 100°C for 30 min, and then treated in a manner similar to that described about to give II (57 mg) as blue plates; mp 231—232°C.

Treatment of XIIIa with Sulfuric Acid. A mixture of XIIIa (60 mg) and concentrated sulfuric acid (1 m*l*) was heated at about 100°C for 40 min, and then diluted with water and extracted with chloroform. The solvent was evaporated, and the residue was chromatographed on an alumina column. The first effluent, when eluted with benzene, gave II (12 mg) as blue plates; mp 231—232°C. The second effluent, when eluted with chloroform, gave XIV (35 mg) as violet plates; mp 189—190°C.

Treatment of XIIb with Hydrobromic Acid. A mixture of XIIb (100 mg) and concentrated hydrobromic acid was heated at about 100°C for 30 min, then diluted with water and extracted with chloroform. The solvent was evaporated, and the residue was chromatographed on an alumina column. The first effluent, when eluted with a 1 : 2 mixture of benzene and cyclohexane, gave II (27 mg) as blue plates; mp 231—232°C. The second effluent, when eluted with benzene-chloroform, gave ethyl 2-phenylazulene-1-carboxylate (XIIIb) (40 mg) as reddish-violet needles; mp 85—86°C.

Found: C, 82.84; G, 6.08%. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84%. UV (MeOH): λ_{max} nm (log ε): 226 (4.27), 308 (4.67), 356 (3.80), 366 (3.81), 550 (2.62).

Treatment of XIIIb with Phosphoric Acid. A mixture of XIIIb (17 mg) and 100% phosphoric acid (0.4 m*l*) was heated at about 100°C for 30 min. Subsequent dilution with water gave II (12 mg) as blue crystals; mp 231—232°C.

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